Origin of magnetite crystals in Martian meteorite ALH84001 carbonate disks

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Background and Introduction: Martian meteorite ALH84001 preserves evidence of interaction with aqueous fluids while on Mars in the form of microscopic carbonate disks which are believed to have precipitated ~3.9 Ga ago at beginning of the Noachian epoch. Intimately associated within and throughout these carbonate disks are nanocrystal magnetites (Fe_3O_4) with unusual chemical and physical properties, whose origins have become the source of considerable debate. One group of hypotheses argues that these Fe_3O_4 are the product of partial thermal decomposition of the host carbonate. Alternatively, the origins of Fe_3O_4 and carbonate may be unrelated; that is, from the perspective of the carbonate the magnetite is allochthonous. We have sought to resolve between these hypotheses through the detailed characterized of the compositional and structural relationships of the carbonate disks and associated magnetites with the orthopyroxene matrix in which they are embedded [1]. We focus this discussion on the composition of ALH84001 magnetites and then compare these observations with those from our thermal decomposition studies of sideritic carbonates under a range of plausible geological heating scenarios.
Methods: *ALH84001*. Seven focused ion beam (FIB) sections were extracted from two carbonate disks **--** three from the disk inner cores and four from the thin rims which surround the cores. Sections were analyzed by high resolution transmission electron microscopy (TEM) equipped with light element energy dispersive X-ray spectroscopy (EDX).
Roxbury Siderite. To investigate the chemical compositions of magnetite formed from the decomposition of Fe-rich carbonates, a sample of Roxbury siderite, having a bulk composition of $(Fe_{0.84}Mg_{0.10}Mn_{0.04}Ca_{0.02})CO_3$ [2], was decomposed using two different heating regimes – 'slow', (~10^{-2} K/sec; identical to that used by [3]), and 'fast' (~10^8-10^9 K/sec) using a pulsed CO_2 laser to simulate the rapid heterogeneous heating. Unheated samples served as controls. Siderite samples were prepared for analysis by TEM using diamond knife ultramicrotomy.
Results: *ALH84001*. Carbonate disks can be envisioned as being composed of three concentric annular zones; the center composed of an inner and outer core surrounded by a thin rim composed of optically alternating black-white-black layers. ALH84001 magnetites are embedded within all compositions of carbonate ranging from the most Fe-rich $(Fe_{0.60}Mg_{0.16}Ca_{0.05}Mn_{0.04})CO_3$ at the disk core to essentially Fe-free magnesite with the highest population density occurring within the black layers of the rim zone. The majority of these magnetites are pure Fe_3O_4 although there were several notable exceptions -- a small fraction of magnetites contained minor to trace amounts of Cr.
Roxbury Siderite Control Sample. Roxbury siderite is compositionally analogous to the Fe-rich component of ALH84001 carbonate disks. However, TEM characterization at the sub-micron scale of Roxbury siderite shows significant variations in Fe:Mg ratio relative to the bulk composition and appeared to be correlated with grain size. The fine grain (<100 nm) component is Mg-poor, while, by comparison, the coarse grained component is Mg-rich.
Roxbury Siderite 'Fast' and 'Slow' Heated Samples. Under both 'fast' and 'slow' heating regimes, decomposition of Roxbury siderite resulted in the formation of impure ferrites with the Mg content of the impure ferrite varying from one crystal to another while the Mn content remained invariant. Since the Mg and Mn variation mirrors that of the unheated carbonate in magnitude and range, this variation is simply a reflection of the initial content of the carbonate. These results, in conjunction with prior carbonate decomposition studies relating to the thermochemistry of the Fe-, Mg- and Ca-ternary carbonates (*e.g*., references compiled in [1]), show that the decomposition of impure, cation substituted siderites invariably yields impure *Fe*-oxides.
Discussion & Implications: Although thermal decomposition hypotheses for the observation of chemically pure magnetites in ALH84001 carbonate disks appears, on the surface, to provide a simple inorganic explanation of the observations, it is not applicable to the formation of the vast majority of ALH84001 magnetites. For example, it is difficult to suggest a process by which the magnesite, which is essentially Fe-free, decomposed to form magnetite. Furthermore, it would be difficult to explain the presence of chemically impure magnetites with minor to trace amounts of Cr since this element cannot substitute into the trigonal ($R\overline{3}c$) structure of carbonate.

Thermal decomposition of Roxbury siderite under <u>*both*</u> 'fast' and 'slow' heating resulted in the formation of impure (Mg,Ca,Mn)-ferrites. These findings agree with prior decomposition studies performed under a wide variety of conditions (see references in [1]) and are in stark contrast to the pure magnetites in ALH84001 carbonate disks.

The presence of chemically pure ALH84001 magnetite is inconsistent with formation by thermal decomposition of the host carbonate. We suggest that the majority of ALH84001 magnetites has an allochthonous origin and was added to the carbonate system from an outside source. This origin does not exclude the possibility that a fraction is consistent with formation by biogenic processes, as proposed in previous studies.

References: [1] Thomas-Keprta, K. et al. (2009) *GCA* **73**, 6631-6677. [2] Lane, M.D. and Christensen, P.R. (1997) *JGR*, 102, 25581-25592. [3] Golden, D.C. et al. (2006) *LPSC XXXVII*, Abst #1199. [4] Treiman, A.H. (2003) *Astrobiology*, 3, 369-392.